

# PATENT SPECIFICATION

DRAWINGS ATTACHED

1.164.418



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## COMPLETE SPECIFICATION

### Improvements in or relating to the Production of a Protective Layer on the Surface of a Semiconductor Body

5 We, SIEMENS AKTIENGESELLSCHAFT, a German Company of Berlin and Munich, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The present invention relates to the production of a protective layer on the surface of a semiconductor body, for example a semiconductor component.

15 It is usual to provide the surface of a semiconductor component with a thin protective layer of silicon oxide. This protective layer is frequently required during the manufacture of the semiconductor component, for example where the so-called planar technique is used, in order to enable a localised diffusing-in of doping substances from the gas phase into the semiconductor crystal to be carried out. Silicon dioxide layers, as is known, have the property that they are impenetrable to a number of the usual doping substances. Consequently, such a protective layer can be used as a mask. Recently, silicon nitride layers have been used as additional protective layer materials.

30 If a protective layer of  $\text{SiO}_2$  is to be produced at the surface of a silicon crystal, then it is possible to obtain this protective layer very simply, by the oxidation of the semiconductor surface. It is considerably more difficult to nitride the semiconductor surface in order to produce a silicon nitride layer. With other semiconductors, for instance with germanium, it is necessary to deposit the material of the protective layer, if this is to be of  $\text{SiO}_2$  or  $\text{Si}_3\text{N}_4$ , from the gas phase, i.e. by the thermal conversion of a reaction gas, e.g. at the heated surface of the semi-

conductor crystal. A number of reaction gases are known which can be used to manufacture an  $\text{SiO}_2$ -layer. Several processes have also been proposed for the manufacture of a protective layer of  $\text{Si}_3\text{N}_4$  at the surface of a semiconductor crystal. 45

One such process is described in our co-pending Application No. 19594/67 (Serial No. 1,134,964). This process for the manufacture of a protective layer of a silicon or germanium nitride on a surface of a semiconductor crystal, preferably consisting of silicon or germanium, or an  $\text{A}^{\text{III}}\text{B}^{\text{V}}$ -compound, by the thermal deposition of the silicon or germanium nitride from the gas phase, is characterised by the use of a reaction gas which consists of 50 of contains a metal-free volatile compound containing nitrogen and silicon or germanium which on heating decomposed to form the required nitride. Our co-pending Application No. 19916/67 (Serial No. 1,134,352) proposes a further process. This Application relates to a process for the manufacture of a protective layer of a nitride of one of the semiconductor elements, silicon, germanium and boron, on a surface of a semiconductor crystal from a reaction gas at the heated surface of the crystal, wherein the reaction gas comprises (a) an at least partially halogenated 55 hydride of the semiconductor element in which free hydrogen atoms may be substituted by alkyl and/or aryl groups and/or amino or alkylamino groups, or a halogenated or alkylamino halogenated silazine, or a corresponding compound of germanium or boron, and (b) a volatile nitrogen-hydrogen compound in which the hydrogen atoms may be at least partially substituted by alkyl and/or aryl groups, and wherein the components (a) and (b) of the reaction gas are mixed to form the reaction 60 65 70 75 80

gas only immediately adjacent to the heated surface of the semiconductor crystal.

It has already been proposed, to use protective layers of both silicon nitride and silicon oxide at the surface of a semiconductor body. By the use of at least two protective layers arranged above one another, of which at least one consists of silicon dioxide and at least one of silicon nitride, the advantages of both protective layers, namely the low term density of an  $\text{SiO}_2$  layer and the good masking action of an  $\text{Si}_3\text{N}_4$ -layer against ion migration from the layer surface, can be combined.

One possibility for the production of such a protective layer at the surface of a crystal consisting of silicon, is first to thermally oxidise the silicon surface to form a silicon dioxide layer, and then to deposit a silicon nitride layer from the gas phase onto the silicon oxide layer, for instance using the process previously described. On the other hand, it is possible to first use a reaction gas which is suitable for the deposition of the silicon nitride layer and then to replace this reaction gas later by a reaction gas which is suitable for the deposition of a silicon dioxide layer.

As the reaction gas for the manufacture of a silicon dioxide layer, a mixture of  $\text{SiCl}_4$  and water vapour (possibly diluted with an inert gas), or a mixture of inert gas and tetraethoxysilane ( $\text{Si}(\text{OCH}_3)_4$ ) can, for example, be used, whilst for the production of the silicon nitride layer the methods described in the Applications mentioned previously can be used, or a mixture of silane ( $\text{SiH}_4$ ) and ammonia can be used.

According to the present invention, there is provided a process for the formation of a protective coating on at least a part of the surface of a semiconductor body by depositing at least one layer consisting of silicon dioxide and at least one layer consisting of silicon nitride at the surface of the semiconductor body from the gas phase, the layers being deposited immediately on one another, wherein during the entire formation process a reaction gas capable of depositing a coherent layer of silicon nitride on the semiconductor body is present, and wherein during a part only of the total formation process there is added to said reaction gas, an oxygen-containing gas or gases capable of reacting with the other gases present to deposit a layer of silicon dioxide in a concentration such that during said part of the formation process, a cohesive layer of silicon dioxide is deposited on the semiconductor body, whereby at least one cohesive layer of silicon nitride and at least one cohesive layer of silicon dioxide are deposited on said semiconductor body at the same position on the surface thereof.

The process in accordance with the invention has the advantage, in comparison to that hitherto used, that no change of the active components of the reaction gas, or of the

carrier gas, is necessary, and that the change from nitride deposition to oxide deposition can be obtained simply by the addition of a further gaseous component or components which is or are free from doping components or indeed components which have a contaminating action, and, after removal of the further component or components from the reaction gas, the deposition of silicon dioxide can again be changed over to the deposition of silicon nitride. The occurrence of additional components in the reaction gas used for the deposition of the silicon dioxide layer, which components might cause damage to silicon nitride layers to be deposited subsequently, and which could thus later have a disadvantageous effect during the deposition of the silicon nitride layer, is thus avoided in the process in accordance with the invention.

If it is remembered that the bond energy of the  $\text{Si}-\text{N}$  bond is 105 Kc/mol, but that of the  $\text{Si}-\text{O}$  bond is 192 kc/mol and thus is almost twice that of the former, it becomes obvious that oxygen is able, with appropriate activation, to break the nitrogen-silicon bond and to take the place of the nitrogen. The selection of the concentration of the oxygen, water vapour, or other reaction gas capable of liberating oxygen to the silicon, and which is to be added to the reaction gas for the purpose of depositing silicon dioxide, can thus be effected without difficulty.

Owing to the much high affinity of oxygen, at temperatures of approximately  $1200^\circ\text{C}$  and in the presence of sufficient quantities of oxygen and/or water vapour and/or of compounds splitting off oxygen or water-vapour, it is possible, even where a reaction gas is present whose active component has already previously been provided with a  $\text{Si}-\text{N}$  bond, to produce pure  $\text{SiO}_2$  layers which no longer contain silicon nitride.

The following substances are of particular importance for use as the reaction gas: silanes, for instance  $\text{SiH}_4$  or halogenated silanes, for instance  $\text{SiCl}_4$ , or alkyl silanes, or aryl silanes, which are mixed with ammonia or another gaseous or readily volatile compound containing hydrogen and nitrogen, such as a volatile amine, if desired, in admixture with an inert carrier gas, such as argon or nitrogen. The substances described in the previously mentioned Applications Nos. 19594/67 (Serial No. 1,134,964) and 19916/67 (Serial No. 1,134,352) can also be used, for example silazones or aminosilanes, which already inherently contain an  $\text{Si}-\text{N}$  bond. All these substances have, for instance, pure oxygen and/or water vapour and/or carbon dioxide, if desired, in admixture with hydrogen, added to them, in order to obtain deposition of silicon dioxide instead of the deposition of the silicon nitride currently being effected. In particular, if a multiple alternation of silicon

nitride and silicon dioxide layers is to be obtained, it is advantageous to operate with a flowing reaction gas. One of the usual epitaxy systems or a tube furnace can be used as the apparatus for carrying out the process.

The invention will now be further described with reference to the drawing, which shows in schematic side section one form of apparatus suitable for carrying out a process in accordance with the invention.

Referring to the drawing, a reaction vessel 1 made of quartz is provided with an inlet line 2 and an outlet line 3 for the reaction gas used. Semiconductor plates 5 which are to be provided with a protective layer, for example semiconductor components, are placed within the vessel 1, for example, as shown, on the floor thereof. The compound or compounds to be used for the manufacture of the silicon nitride layers, in admixture with an inert gas, for instance nitrogen, flows into the vessel 1 from a supply vessel 4 through the line 2. In order to heat the plates 5, a heating device, for example, as shown in the drawing, an electric heating plate 6, is provided which, as in the case of the example illustrated, can be arranged outside the reaction chamber. The temperature to be used is adjusted in accordance with special considerations connected, in particular, with the phase of the manufacturing process under consideration. For instance, silicon monocrystals to be provided in accordance with the invention with a protective coating for the purposes of a subsequent diffusion step, can be exposed to far higher temperatures (650 to 1200° C) than can completed semiconductor components which are to be given a final coating with the protective layers. If it is desirable to operate with particularly low temperatures, then the reaction gas may be activated at the surface of the semiconductor crystal to be coated by means of a low temperature electrical gas discharge, for instance, a glow discharge.

A further supply vessel 7 is provided for the silicon oxide deposition which, for example, contains oxygen which can be added at will to the reaction gas flowing from the container 4 into the reaction vessel 1.

Descriptions of the manufacture of the silicon nitride layer can, for example, be found in our co-pending Applications Nos. 19594/67 (Serial No. 1,134,964) and 19916/67, (Serial No. 1,134,352) previously mentioned. The conditions described therein can also be used for the deposition of the silicon nitride layers in the process of the present invention, and can be used without any modification.

If, instead of the silicon nitride layers, silicon dioxide layers are required, then it is merely necessary to add the appropriate quantity of oxygen-containing or yielding gas to the reaction gas, whilst the other deposition conditions remain unchanged. The necessary quantities are determined on the basis of

stoichiometric considerations, which naturally lead to slightly different results, depending upon the type of reaction gas to be used. Normally, however, careful measuring of the oxygen content is not necessary, since the gases in question are used in a highly dilute state and it is not difficult to obtain an excess of oxidising gas.

By a more or less rapid cutting off of the supply of the oxidising components, the changeover from oxide to nitride layers and *vice-versa* can be effected slowly or abruptly.

The protective coatings consisting partially of silicon dioxide and partially of silicon nitride, formed by the process of the invention on the surface of a semiconductor body, are able to effectively protect the semiconductor surface from the electrical point of view, e.g. against disturbing influences from the atmosphere. Such protective coatings possess a further use as diffusion masks in the production of semiconductor arrangements, in particular using the planar technique. In carrying out a production process of this kind, the semiconductor surface is covered with a layer of silicon dioxide ( $\text{SiO}_2$ ) and/or a layer of silicon nitride ( $\text{Si}_3\text{N}_4$ ) and one or more windows extending through to the semiconductor surface are produced or left free in the protection layers. The semiconductor surface prepared in this way is then exposed to the effects of a doping gas, for example to the effects of boron or phosphorus vapour. Whilst these doping materials can without difficulty penetrate at the exposed part of the surface into the interior of the semiconductor body and there produce the desired doping effect, this is impossible at the portions of the semiconductor surface masked with the protective coating. Layers of silicon dioxide ( $\text{SiO}_2$ ) or silicon nitride ( $\text{Si}_3\text{N}_4$ ) have a definite limiting effect on the penetration of the doping material into the parts of the semiconductor surface masked by them, even when the thickness of the protection layers is only a few microns. A silicon nitride layer is generally more effective in preventing doping materials from penetration into the masked semiconductor layer, than a silicon dioxide layer. On the other hand silicon oxide layers in the finished semiconductor arrangement possess a better protective action. For this reason, the combined use of protective layers of silicon dioxide and silicon nitride is extremely useful, the other layer, however, generally being a silicon dioxide layer. After the production of the silicon nitride layer, it is, however, necessary in each case to etch into this layer the windows necessary for the diffusion. However, the silicon nitride produced above 800° C can be etched only with known etching means which will also attack and destroy an etching mask consisting of a photolacquer or the like. A further layer consisting of silicon dioxide ( $\text{SiO}_2$ ) is therefore applied on the



silicon nitride layer. On this layer is deposited a mask of photolacquer and then at the required diffusion windows, the  $\text{SiO}_2$  layer is etched away as far as the nitride layer beneath, and then, in a further operation, the  $\text{SiO}_2$  mask so formed is used for the localised etching of the  $\text{Si}_3\text{N}_4$ -layer situated beneath it, using hot orthophosphoric acid as etching means.

Thus, initially, a  $\text{Si}_3\text{N}_4$ -layer is deposited and then on this a  $\text{SiO}_2$ -layer is deposited, the surface of the  $\text{SiO}_2$ -layer is covered with a photolacquer, this photo-lacquer is locally exposed to light and developed so as to expose the surface of the  $\text{SiO}_2$ -layer at the position or positions where a diffusion window or windows is or are to be formed, the surface of the  $\text{SiO}_2$ -layer so exposed is etched down to the  $\text{Si}_3\text{N}_4$ -layer, using an etching means capable of dissolving  $\text{SiO}_2$  and which does not destroy the photolacquer layer, and the parts of the surface of the  $\text{Si}_3\text{N}_4$ -layer so exposed are etched away as far as the semiconductor surface by means of hot phosphoric acid at the positions not protected by the remaining parts of the  $\text{SiO}_2$ -layer.

The protective coating mask produced in this way is used in the usual way as a diffusion mask in the production of crystal diodes, transistors and other semiconductor components, in particular in accordance with the planar technique.

#### WHAT WE CLAIM IS:—

1. A process for the formation of a protective coating on at least a part of the surface of a semiconductor body by depositing at least one layer consisting of silicon dioxide and at least one layer consisting of silicon nitride at the surface of the semiconductor body from the gas phase, the layers being deposited immediately on one another, wherein during the entire formation process a reaction gas capable of depositing a coherent layer of silicon nitride on the semiconductor body is present, and wherein during a part only of the total formation process there is added to said reaction gas, an oxygen-containing gas or gases capable of reacting with the other gases present to deposit a layer of silicon dioxide in a concentration such that during said part of the formation process, a cohesive layer of silicon dioxide is deposited on the semiconductor body, whereby at least one cohesive layer of silicon nitride and at least one cohesive layer of silicon dioxide are deposited on said semiconductor body at the same position on the surface thereof.

2. A process as claimed in Claim 1 wherein oxygen and/or water-vapour and/or a substance or substances which will form oxygen or water-vapour at elevated temperature, is or are added to the reaction gas to form said silicon dioxide layer or layers.

3. A process as claimed in Claim 1 or Claim 2 wherein the reaction gas consists of or includes silazone or aminosilane, or a mixture of silane, a halogenated silane, an alkyl silane, or an aryl silane, with a gaseous or volatile nitrogen compound.

4. A process as claimed in Claim 3, wherein said nitrogen compound is ammonia, or a volatile amine.

5. A process as claimed in any one of the preceding Claims, wherein the deposition of said layers from the gas phase is effected by heating the semiconductor body.

6. A process as claimed any one of Claims 1 to 4, wherein the reaction gas is activated by means of a low temperature electrical gas discharge.

7. A process as claimed in Claim 6, wherein said electrical gas discharge is a glow discharge.

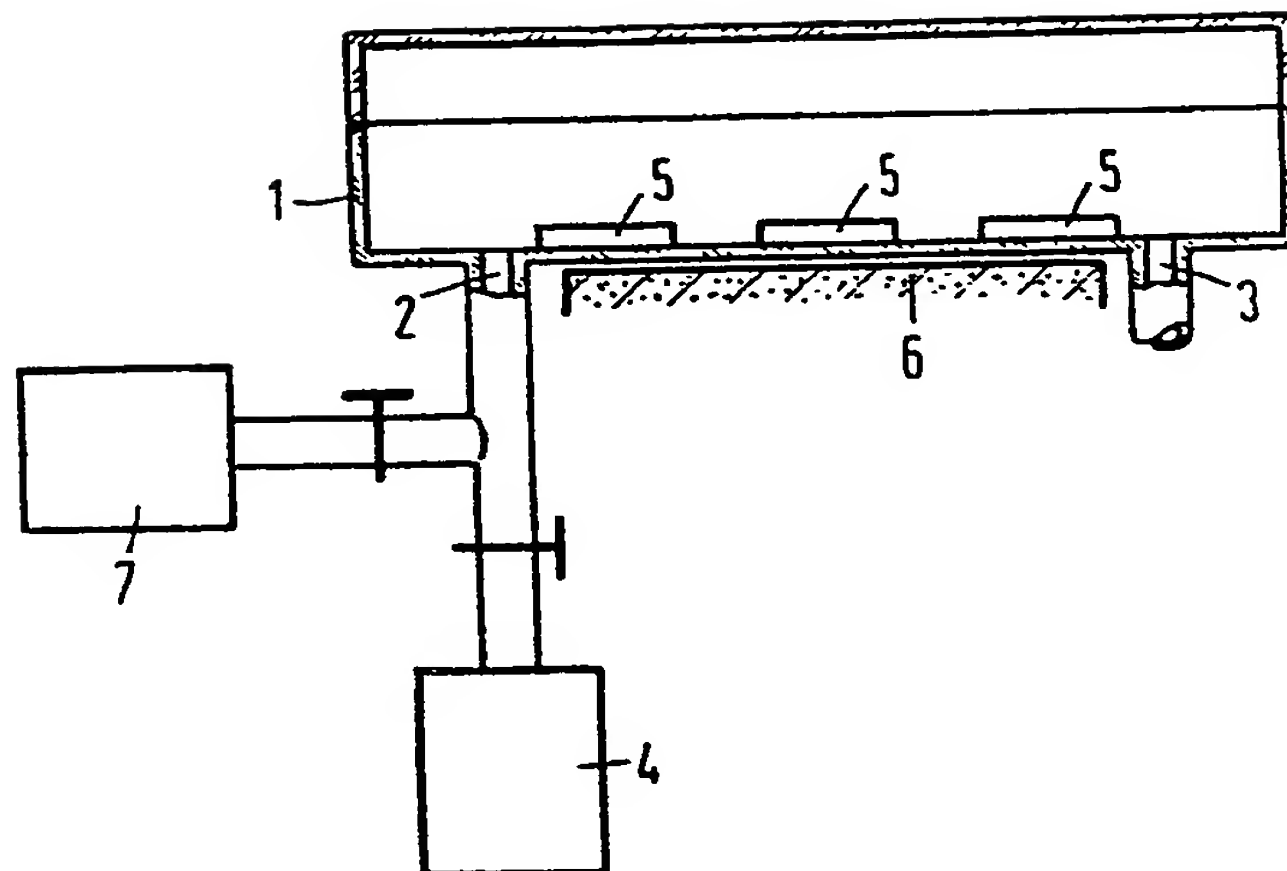
8. A process for the formation of a protective coating on at least a part of the surface of a semiconductor body substantially as hereinbefore described with reference to the drawing.

9. A process as claimed in any one of the preceding Claims, wherein the protective coating also serves as a diffusion mask, and wherein initially a layer of silicon nitride is deposited on the surface of the semiconductor body, a layer of silicon dioxide is deposited on this layer, a layer of a photolacquer is deposited on the silicon dioxide layer, the photolacquer layer is locally exposed to light and developed so as to expose the surface of the silicon dioxide layer at the position or positions where a diffusion window or windows is or are to be formed, the silicon dioxide layer so exposed is etched away down to the silicon nitride layer using an etching means capable of dissolving silicon dioxide but which will not destroy the photolacquer layer, and the silicon nitride layer so exposed is etched away down to the semiconductor surface using hot phosphoric acid as etching medium, at the part or parts not protected by the residual silicon dioxide layer.

10. A semiconductor body having a protective coating on at least a part of the surface thereof formed by a process as claimed in any one of Claims 1 to 9.

11. A semiconductor component having a protective coating on at least a part of the surface thereof formed by a process as claimed in any one of Claims 1 to 9.

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